Transactions of the Materials Research Society of Japan 32[3] 759-762 (2007)

Preferential Synthesis of Cyclic Phenylazomethines and Their Redox Behavior

Ryo Shomura, Masayoshi Higuchi* and Dirk G. Kurth
National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044 Japan
Fax: 81-029-860-4721, e-mail: HIGUCHI.Masayoshi@nims.go.jp

We synthesized cyclic phenylazomethines *via* dehydration of aromatic amines with aromatic ketones in the presence of titanium tetrachloride as a Lewis acid. Stepwise synthesis of a cyclic tetramer of phenylazomethine was also successful. Protonation behavior of the cyclic tetramer was investigated using UV-vis spectral measurements. The cyclic tetramer itself is not redox-active, but a reversible redox wave appeared in cyclic voltammograms when protonated in the presence of trifluoroacetic acid. We revealed that the redox potential is controlled by the concentration of the acid.
Key words; Cyclic phenylazomethine, protonation, UV-visible, redox, Cyclic voltammetry

1. INTRODUCTION

Organic-metallic hybrid polymers have received much attention to their unique electrochemical, photochemical, and magnetic properties, which are caused by strong interaction between organic modules and metal ions.[1] One way to obtain hybrid polymers is taking advantage of complexation of metal ions with organic modules having two coordination sites such as bis(terpyridyl)benzene.[2] The other is metal ion assembly to organic macromolecular modules bearing many coordination sites such as polypyridines. Polyphenylazomethines, which have many imines with high coordination ability for metal ions, seem to be useful as the macromolecular modules, but poor solubility of the polymers prevents the applications as an organic module.[3]

On the other hand, we recently synthesized dendritic phenylazomethines as a unique topological polymer, and found that they have high solubility to chloroform, based on less intermolecular stacking between the polymer chains.[4] This finding indicates that creation of novel polyphenylazomethines with a non-linear structure is effective to use polyphenylazomethines as an organic module of organic-metallic hybrid polymers. We herein report synthesis of cyclic phenylazomethines and the redox behavior in the presence of trifluoroacetic acid.

2. EXPERIMENTAL SECTION

2.1 General Procedures

Methanol, ethanol, dioxane, acetic acid, DMSO and DMF were dehydrated, and were purchased from Wako or Kanto Chemical Co. Inc. De-ionized H_2O was used in the experiment where required. ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a JEOL AL 300/BZ instrument. Chemical shifts were given relative to TMS. Mass spectra (MS) were measured by using AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. High resolution mass spectra (HRMS) were measured by using Shimadzu LCMS-IT-TOF spectrometer. UV/vis spectra were obtained by using a Shimadzu UV-2550 UV-visible spectrophotometer. Cyclic voltammetry (CV) were measure on a electrochemical analyzer, ALS/H CH instruments, with a platinum wire counter electrode and Ag/AgCl reference electrode in an anhydrous and argon saturated 0.1 mol L^{-1} acetonitrile solution of tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4). The polymers were coated on a carbon working electrode for DPV, and an ITO plate for amperometric experiments from dilute MeOH solutions. Analytical thin layer chromatography (TLC) was Merck aluminium oxide 60 F_{254} neutral or silica gel 60 F_{254} coated on 25 TCC aluminium sheets (20 x 20 cm). Flash column chromatographic separations were performed on silica gel 60 N (neutral, 40-100 μM), Kanto Chemical Co. Inc., or activated alumina oxide (75 μM), Wako.

2.2 Synthesis of cyclic tetramers of phenylazomethine

As a typical synthetic procedure on cyclic phenylazomethines, we show synthesis of **CPA-A**. 1,4-Dibenzoylbenzene (1.00 g, 3.49 mmol), 4,4'-diaminophenylmethane (692 mg, 3.49 mmol), and DABCO (2.35 g, 21.0 mmol) were dissolved in chlorobenzene (200 ml). $TiCl_4$ (994 mg, 5.24 mmol), dissolved in 5 ml of chlorobenzene, was added dropwise to the solution. The reaction mixture was heated in an oil bath at 150 °C for 3 h. After cooling to room temperature, $TiCl_4$ (994 mg, 5.24 mmol), dissolved in 5 ml of chlorobenzene, was added dropwise to the solution and DABCO (2.35 g, 21.0 mmol) were added to the reaction mixture, and the solution was heated again at 150 °C for 3 h. After cooling again, 4,4'-diaminophenylmethane (346 mg, 1.75 mmol), $TiCl_4$ (994 mg, 5.24 mmol), dissolved in 5 mL of chlorobenzene, was added dropwise to the solution and DABCO (2.35 mg, 21.0 mmol) were added to the reaction mixture, and the solution was heated again at 150 °C for 12 h. After checking the disappearance of the starting material on TLC, the precipitate was removed by filtration. The filtrate was concentrated, and **CPA-A**, was isolated by gel permeation chromatography (241 mg, 17.5 %). *Spectral data*: ^1H NMR (300 MHz, $CDCl_3$): δ= 7.80 (d, J = 7.8 Hz, 4H), 7.58 (d, J = 8.4 Hz, 4H), 7.46 (t, J = 7.8 Hz, 2H), 7.42 (dd, J = 7.8, 7.8 Hz, 4H), 7.24 (t, J = 7.8 Hz, 2H), 7.21 (dd, J = 7.8, 7.8 Hz, 4H), 7.06 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 7.8 Hz, 4H), 6.88 (d, J = 8.4 Hz, 4H), 6.64 6.88 (d, J = 8.4 Hz, 4H), 6.61 6.88 (d, J = 8.4 Hz, 4H), 6.53 6.88 (d, J = 8.4 Hz, 4H), 3.77 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 68.95, 167.31, 150.07,

149.11, 139.35, 138.95, 138.82, 137.04, 136.09, 135.71, 130.93, 129.50, 129.46, 129.39, 129.25, 129.10, 128.96, 128.48, 128.39, 128.31, 127.99, 120.73, 40.29; IR (KBr, cm-1): 1631 (C=N), 1610 (phenyl), 1593, 1499, 701; HRMS (LCMS-IT-TOF-MS): Calcd 897.3952; Observed 897.3943.

2.3 Stepwise synthesis of **CPA-A**

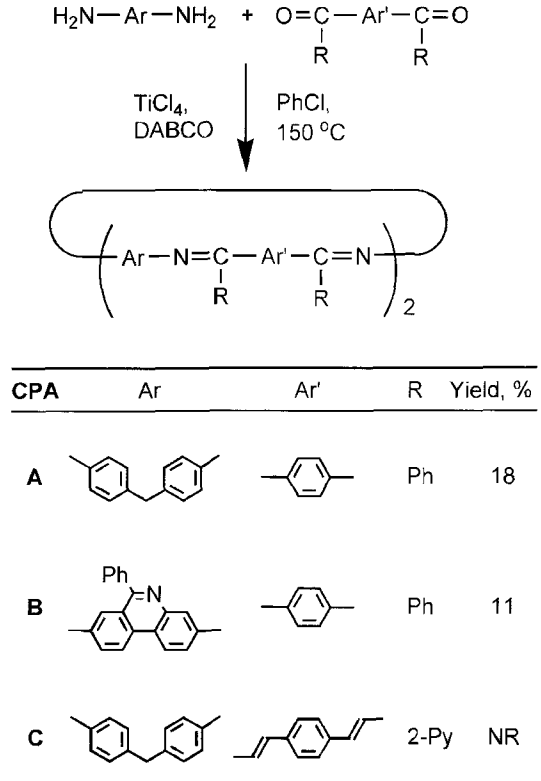
1,4-Dibenzoylbenzene (28.9 g, 101 mmol), 4,4'-diaminophenylmethane (2.0 g, 10.1 mmol), and DABCO (13.6 g, 121.1 mmol) were dissolved in chlorobenzene (1.2 L). $TiCl_4$ (5.74 g, 30.3 mmol), dissolved in 5 ml of chlorobenzene, was added dropwise to the solution. The reaction mixture was heated at 150 °C for 12 h. After cooling to room temperature, the precipitate was removed by filtration. The filtrate was concentrated, and diketon **D** was isolated by silica gel chromatography (1.2 g, 16 %). Diketone **D** was identified by TOF-MS. *Spectral data*: MALDI-TOF-MS: Calcd for $C_{53}H_{38}N_2O_2$: ($M+H^+$) 735.29, found: m/z 735.44.

4,4'-Diaminophenylmethane (46.6 mg, 0.24 mmol), diketone **D** (354 mg, 0.47 mmol), and DABCO (316 mg, 2.82 mmol) were dissolved in chlorobenzene (200 ml). $TiCl_4$ (134 mg, 0.71 mmol), dissolved in 5 ml of chlorobenzene, was added dropwise to the solution. The reaction mixture was heated at 150 °C for 2 h. After cooling, 4,4'-diaminophenylmethane (93.2 mg, 0.47 mmol), $TiCl_4$ (134 mg, 0.71 mmol) dissolved in 5 mL of chlorobenzene, and DABCO (316 mg, 2.82 mmole) were further added in the reaction mixture, and the solution was heated again at 150 °C for 12 h. After cooling again, 4,4'-diaminophenylmethane (46.6 mg, 0.24 mmol), $TiCl_4$ (134 mg, 0.71 mmole) dissolved in 5 ml of chlorobenzene, and DABCO (316 mg, 2.82 mmol) were further added to the reaction mixture, and the solution was heated again at 150 °C for 2 h. After checking the disappearance of the starting material on TLC, the precipitate was removed by filtration. The filtrate was concentrated by evaporation, and **CPA-A** was isolated by silica gel chromatography and gel permeation chromatography (299 mg, 71 %).

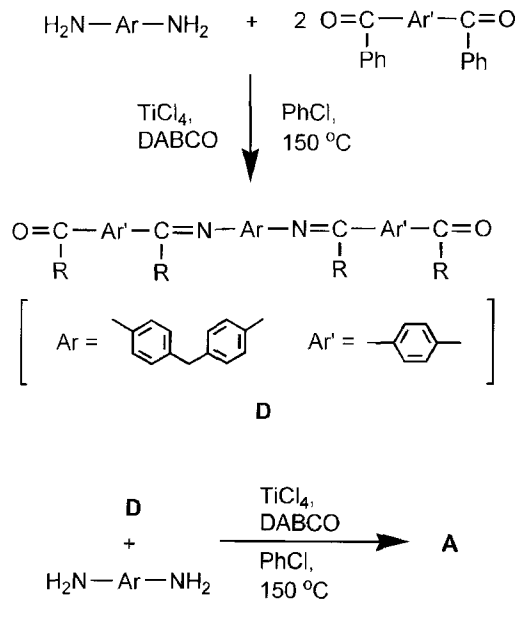
3. RESULT AND DISCUSSION

3.1 Synthesis of cyclic phenylazomethines

In general, dehydration of aromatic diamines with aromatic diketones in the presence of $TiCl_4$ and 1,4-diazabicyclo[2.2.2]octane (DABCO) resulted in formation of a linear structure of polyphenylazomethines. On the other hand, we found that cyclic phenylazomethines are preferentially obtained when we use diketones substituted with phenyl groups at a α-position of the ketones, because of the formation of *cis*-conformational azomethines based on the steric hindrance of the bulky phenyl groups. We investigated the cyclization using some diketone and diamine monomers shown in Scheme 1 An excess amount of $TiCl_4$, DABCO, and aromatic diamines with respect to the aromatic diketones were used because of the higher yield for the cyclic product and less for the acyclic one, which simplified purification process by silica gel column and GPC. Cyclic tetramers having diphenylmethane and phenylphenanthridine (**CPA-A** and **-B**) were isolated in 18 and 11% yields, respectively, via dehydration of the corresponding monomers. On the other hand, when diketone with pyridine rings was used as a monomer, no reaction proceeded. It is probably due to low reactivity of the diketone monomer bearing pyridine groups.



Scheme 1. Synthesis of cyclic phenylazomethine tetramers.



Scheme 2. Stepwise synthesis of **CPA-A**.

3.2 Stepwise synthesis of **CPA-A**

Next we tried stepwise synthesis of **CPA-A** in order to enhance the yield in cyclization step (Scheme 2). Diketone **D** was obtained in a 16% yield by using a ten times amount of the diketone monomer with respect to

the diamine monomer. Then we succeeded to obtain **CPA-A** in a 71% yield *via* dehydration of diketone **D** with the diamine monomer. The yield is extremely high as a yield of a cyclic oligomer with a single degree of polymerization during general polymerizations.

3.3 UV-vis spectral change during protonation of **CPA-A**

Since coordination chemistry of the azomethines has been well-established, the protonation is easily confirmed by the color change from yellow to orange in solution. During the titration of **CPA-A** with trifluoroacetic acid (TFA), a new absorption around 310nm attributed to π-π* transition of protonated azomethines emerged, and absorption at 260nm based on the original π-π* transition of azomethines disappeared in the UV-vis spectra (Figure 1).

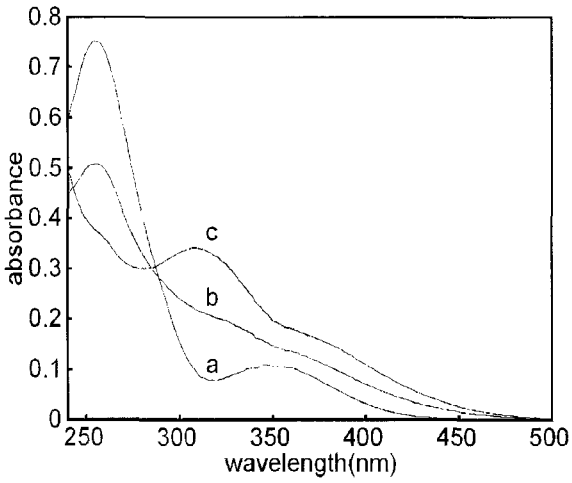


Figure 1. UV-vis spectral changes of **CPA-A** during addition of (a) 0, (b) 200, (c) 2000 equivalents of trifluoroacetic acid. (Solvent: dichloromethane / acetonitrile = 1:1, [CPA-M] = 10 mM).

3.4 Redox properties of protonated **CPA-A**

CPA-A itself is not redox-active, but the reversible redox wave was clearly observed in cyclic voltammograms when **CPA-A** was protonated. The protonated **CPA-A** shows a single redox wave at -0.5V vs Ag/Ag^+ (Figure 2). Notably, the redox potential depends on the concentration of TFA. The concentration dependency obeys the Nernst equation (inset Figure 2. Slope: 60 mV / log [TFA]). The peak separation is smaller than 60 mV, indicating a multi-electron transfer process.[5] Presumably, the reversible electrochemistry is observable a result of stable redox species.

4. CONCLUTION

For development of organic-metallic hybrid materials, it is essential to create novel organic modules with metal assembling functions. We synthesized cyclic phenylazomethines as an organic module, and succeeded the preferential cyclization by using stepwise synthesis. Protonation behavior of the cyclic tetramer was investigated using UV-vis spectral measurements. We found that the protonated cyclic tetramer is redox-active, and the redox potential is controlled by the concentration of the acid. These fundamental results are surely useful to reveal their complexation behavior with metal ions.

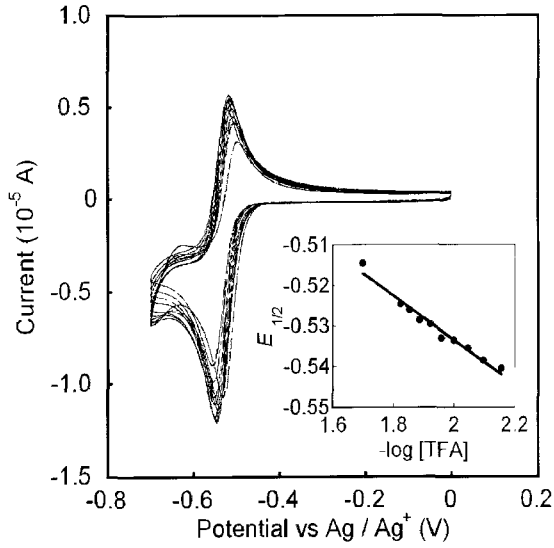


Figure 2. Cyclic voltammograms of **CPA-A** (0.25 mM) in 0.2 M $TBABF_4$ / acetonitrile in the presence of trifluoroacetic acid (7.0-20.0 mM). (Scan rate: 100 mV/S; electrode: carbn disk). Inset: Concentration dependent potential (Slope: -60 mV / -log [TFA]).

REFERENCES

[1] (a) T. Yasuda, I. Yamaguchi, and T. Yamamoto, *Adv. Mater.*, **15**, 293-296 (2003). (b) K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, and H. Chiba, *Nature*, **415**, 509-511 (2002). (c) U. Kolb, K. Büscher, C. A. Helm, A. Lindner, A. F. Thünemann, M. Menzel, M. Higuchi, and D. G. Kurth, *Proc. Natl. Acad. Sci. USA*, **103**, 10202-10206 (2006).

[2] (a) P. R. Andres and U. H. Schubert, *Adv. Mater.*, **16**, 1043-1068 (2004). (b) C. N. Carlson, C. J. Kuehl, R. E. Da-Re, J. M. Veauthier, E. J. Schelter, A. E. Milligan, B. L. Scott, E. D. Bauer, J. D. Thompson, D. E. Morris, and K. D. John, *J. Am. Chem. Soc.*, **128**, 7230-7241 (2006). (c) P. P. Lainé, F. Bedioui, F. Loiseau, C. Chiorboli, and S. Campagna, *J. Am. Chem. Soc.*, **128**, 7510-7521 (2006). (d) K. Sénéchal-David, J. P. Leonard, S. E. Plush, and T. Gunnlaugsson, *Org. Lett.*, **8**, 2727-2730 (2006). (e) E. Coronado, J. R. Galán-Mascarós, C. Marti-Gastaldo, E. Palomares, J. R. Durrant, R. Vilar, M. Grätzel, and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, **127**, 12351-12356 (2005).

[3] (a) A. A. Volpe, J. C. Carson Jr., and L. G. Kaufman, *Thermochim. Acta*, **2**, 175 (1971). (b) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966). (c) P. A. Williams, K. A. Ellzey, A. B. Padias, and H. K. Hall Jr., *Macromolecules*, **26**, 5820 (1993).

[4] (a) M. Higuchi, M. Tsuruta, H. Chiba, S. Shiki, and K. Yamamoto, *J. Am. Chem. Soc.*, **125**, 9988 (2003). (b) M. Higuchi, H. Kanazawa, and K. Yamamoto, *Org. Lett.*, **5**, 345 (2003). (c) M. Higuchi, R. Shomura, Y. Ohtsuka, A. Hayashi, K. Yamamoto, and D. G. Kurth, *Org. Lett.*, **8**, 4723 (2006).

[5] (a) D. H. Evans and K. Hu, *J. Chem. Soc. Faraday Trans.*, **92**, 3983 (1996). (b) K. Hu and D. H. Evans, *J. Electroanal. Chem.*, **423**, 29 (1997). (c) P. F. Hapiot, L. D. Kispert, V. V. Konovalov, and J. M. Saveant, *J. Am. Chem. Soc.*, **123**, 6669 (2001). (d) T. Nishiumi, Y. Chimoto, Y. Hagiwara, M. Higuchi, and K. Yamamoto,

Macromolecules, **37**, 2661 (2004).

(Received December 30, 2006;Accepted March 14, 2007)